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(54) Title: THERMOPLASTIC MOULDING COMPOSITIONS AND POLYMER ADDITIVES

(57) Abstract

A polymer additive is described for addition to a thermoplastic moulding composition comprising polyethylene terephthalate or a copolyester thereof so as to effect reduction of the level of acetaldehyde resulting after processing thereof, said polymer additive comprising a hydroxylic compound selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy groups, and cycloaliphatic hydroxilic compounds containing at least two hydroxy groups, uniformly distributed in a polyester-compatible organic liquid carrier. The invention further relates to the use of a hydroxylic compound selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy groups, and cycloaliphatic hydroxylic compounds containing at least two hydroxy groups, as an additive to a thermoplastic moulding composition for the reduction of the amount of acetaldehyde formed upon subjecting said moulding composition to melt processing. Thermoplastic moulding compositions, processes using same and preforms and bottles made therefrom are also described. Preferred hydroxylic compounds include triglycerin, trimethylolpropane, dipentaerythritol, tripentaerythritol, D-mannitol, D-sorbitol, and xylitol.

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THERMOPLASTIC MOULDING COMPOSITIONS AND POLYMER ADDITIVES

This invention relates to polymer additive compositions and their use. In particular it relates to an additive composition and its use for addition to thermoplastic moulding compositions comprising polyesters, such as polyethylene terephthalate.

Polyethylene terephthalate is used on a large scale for the manufacture of food packages such as bottles. Such bottles are widely utilised for packaging of beverages, such as carbonated soft drinks, beer, or mineral water. Whilst some beverage bottlers prefer clear non-pigmented bottles, others prefer coloured bottles. Particularly in the case of bottles intended for holding carbonated drinks, a sandwich construction is used in which nylon or an ethylene/vinyl alcohol resin is incorporated in a multi-layer preform with polyethylene terephthalate in order to improve the gas barrier properties of the bottles. It has also been proposed, for the same purpose, to admix a polyamide with the polyethylene terephthalate since the presence of the polyamide provides gas barrier properties.

The technique commonly used to manufacture bottles from moulding compositions comprising polyethylene terephthalate generally involves a two stage process. In the first stage granules of the moulding composition are injection moulded to make a preform. In the second stage the preform is blow moulded to the desired shape.

In such a process the polyethylene terephthalate is typically post-condensed and has a molecular weight in the region of about 25,000 to 30,000. However, it has also been proposed to use a fibre grade polyethylene terephthalate, which is cheaper but is non-post-condensed, with a lower molecular weight in the region of about 20,000. It has further been suggested to use copolyesters of polyethylene

terephthalate which contain repeat units from at least 85 mole % terephthalic acid and at least 85 mole % of ethylene glycol. Dicarboxylic acids which can be included, along with terephthalic acid, are exemplified by phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, and sebacic acid. Other diols which may be incorporated in the copolyesters, in addition to ethylene glycol, include diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentane-2,4-diol, 2-methylpentane-1,4-diol, 2,2,4-trimethylpentane-1,3-diol, 2-ethylhexane-1,3-diol, 2,2-diethylpropane-1,3-diol, hexane-1,3-diol, 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and 2,2-bis-(4-hydroxypropoxyphenyl)-propane. In this specification the term "polyethylene terephthalate" includes not only polyethylene terephthalate but also such copolyesters.

If the eventual bottle is to be coloured, then it is conventional to admix a pigment or pigments with the polyethylene terephthalate granules charged to the hopper of the injection moulding machine used to make the bottle preform. For this purpose the pigment or mixture of pigments can be added as a solid concentrate or in powder form or as a dispersion in a liquid carrier. Such liquid carriers are generally inert materials such as hydrocarbon oils, esters, alcohols, or a mixture of two or more thereof. Any such liquid carrier must be selected so as to have good compatibility with polyethylene terephthalate and, if the pigment is to be dissolved, also good solvent properties for

the pigment or pigments. In addition, if the moulding composition is to be used for manufacture of food packages, the carrier must be non-toxic. Moreover the quantity of carrier used should desirably be kept to a minimum so as not to affect adversely the properties of the polyethylene terephthalate in the preform or bottle.

The softening point of polyethylene terephthalate is high. Thus a typical temperature needed for processing of polyethylene terephthalate is in the region of 260°C to 285°C. A recognised problem in the industry is that, under the high temperatures and shear conditions needed for injection moulding to make a preform and for blow moulding of the preform to make a bottle, polyethylene terephthalate tends to degrade, resulting in the formation of acetaldehyde. The presence of acetaldehyde in the material of the finished bottle is undesirable, particularly when the bottle is to be used for products for human consumption, because the acetaldehyde can migrate from the walls of the package or bottle into its contents, whereupon it adversely affects the flavour and fragrance properties of the comestible product. Although the migration of acetaldehyde from a polyethylene terephthalate bottle into a carbonated drink is undesirable, a trace of acetaldehyde can often be tolerated because the taste and fragrance of the drink are not usually noticeably affected. However, the presence of even minute amounts of acetaldehyde in a non-carbonated drink, such as still mineral water, tends to impart a most undesirable adverse taste and odour to the drink.

Methods for measurement of acetaldehyde in industrially injection-moulded polyethylene terephthalate preforms have been described by F. Villain *et al.*, Journal of Polymer Science, Vol. 52, 55-60 (1994).

Attempts have been made by equipment manufacturers to

modify the design of the processing machinery so as to enable the intensity of the processing conditions needed to make the bottle preforms and for blow moulding thereof to be reduced. In this way it is hoped that the formation of acetaldehyde in the course of the high temperature processing conditions can be minimised.

The use of vented extruders to devolatilise polymers has been disclosed, for example, in United States Patent No. 5,597,891, which teaches a process for producing reduced acetaldehyde polyester articles by using a purge gas in a vented extruder to remove acetaldehyde. United States Patent No. 5,102,594 discloses thermoplastic condensation polymer supplied to a vented extruder in powdered form.

In Swiss Patent No. 655,938 there is described a procedure for preparing high molecular weight polyethylene terephthalate containing less than 5 ppm dissolved and bound acetaldehyde which involves treatment of the polyethylene terephthalate with a pure alcohol or alcohol/water mixture at a temperature of at least 130°C followed by post-condensation at 240°C to 245°C in an inert gas or under vacuum.

Another approach that has been attempted is to use additives which will react with the acetaldehyde as it is formed. However, it is important that any additive used should not adversely affect the properties of the bottle or other final product. In particular it is important not to add a material which can impart undesirable haze or colour. Thus in a paper by F. Villain *et al.*, Polymer Degradation and Stability, 49, 1995, 393-397, it is proposed to incorporate additives in polyethylene terephthalate in order to minimise the amounts of acetaldehyde and formaldehyde produced during the injection moulding process. Various stabilising additives were tested by these authors including terephthalic acid, phthalimide, dimethyl terephthalate, 4-hydroxybenzoic

acid, 5-hydroxyisophthalic acid, 3,5-dihydroxybenzoic acid, phenyl isocyanate, phthalic anhydride, 4-aminobenzoic acid, resorcinol, and diphenylamine. They reported that, when used in an injection machine at a weight percentage of 1% based upon the weight of polyethyiene terephthalate, 4-aminobenzoic acid, 3,5-dihydroxybenzoic acid and diphenylamine were found to be the most effective additives under laboratory conditions. These authors further postulated that 4-aminobenzoic acid acts as both a free radical scavenger and a hydroxyethyl chain blocker.

United States Patent No. 5,258,233 describes polyester/polyamide blends which have gas barrier properties and through reduction of acetaldehyde concentration in the polyester improve the storage properties of foodstuffs over previously reported blends. The use of low molecular weight partially aromatic polyamides having a number average molecular weight of less than 15,000 or low molecular weight aliphatic polyamides having a number average molecular weight of less than 7,000 is said to be more effective in reducing residual acetaldehyde in polyethylene terephthalate based polyesters than high molecular weight polyamides. However, a recognised problem associated with utilising a polyamide as an additive in polyethylene terephthalate formulations is that it causes discolouration of the preform due to degradation during the melt extrusion process.

International Patent Publication No. WO 94/29378 teaches a polyester/zeolite admixture which is said to have an excellent gas barrier property and an improved flavour retaining property as well as clarity. Addition of small- or medium-pore zeolites in a critical amount to a polyester is said to reduce the concentration of acetaldehyde in the polyester without producing haze.

In International Patent Publication No. WO 98/18848

there is proposed a process for producing moulded articles comprising the steps of:

a) melt reacting at least one glycol and at least one dicarboxylic acid to form a polyester having an I.V. (inherent viscosity) of at least about 0.5 dl/g, wherein said at least one glycol is selected from the group consisting of glycols having up to 10 carbon atoms and mixtures thereof and said dicarboxylic acid is selected from the group consisting of alkyl dicarboxylic acids having 2 to 16 carbon atoms, aryl dicarboxylic acids having 8 to 16 carbon atoms and mixtures thereof in the presence of a catalyst which is substantially free from Co compounds;

b) adding an acetaldehyde reducing additive to said polyester to form a reduced acetaldehyde polyester; and

c) forming said reduced acetaldehyde polyester into shaped articles directly from step b.

Such a process can thus be operated as a "melt-to-mould" process. As acetaldehyde reducing additive there can be used any additive known to reduce acetaldehyde. Recommended additives for this purpose include polyamides, polyesteramides, nylon-6 and other aliphatic polyamides, ethylenediaminetetraacetic acid, alkoxylated polyols, bis(4-β-hydroxyethoxyphenyl)-sulphone, zeolite compounds, 5-hydroxyphthalic acid, poly(ethylene isophthalate), supercritical carbon dioxide, and protonic acid catalysts. Other known scavengers such as polyethyleneimine may also be used.

Another approach, which is described in United States Patent No. 4,361,681, involves capping of the hydroxyl end

succinic anhydride or phthalic anhydride. The use of pyromellitic anhydride for end capping of polyethylene terephthalate has been proposed in United States Patent No. 5,243,020.

European Patent Publication No. 0 878 502 A discloses a stabiliser mixture for thermally stabilising organic polymers, especially food packages, consisting of (1) α-tocopherol, (2) a solid polyhydroxy compound which is selected from the group consisting of triglycerin, ditrimethylolpropane, dipentaerythritol, tripentaerythritol, D-mannitol, D-sorbitol, and xylitol or (3) an acid binding material or a mixture of components (2) and (3). Amongst the polymers which can be thermally stabilised in this way are said to be polyesters, including polyethylene terephthalate. However, no experimental evidence is provided which involves use of polyethylene terephthalate.

United States Patent No. 5,250,333 proposes polyethylene terephthalate modified by incorporation in the polymer structure of an alkoxylated polyol, such as ethoxylated trimethylolpropane. The modified polyethylene terephthalate is described as melt strength enhanced and extrusion blow mouldable and is said to be useful for making bottles or containers having hot fill applications. Reduced yellowness is said to be provided.

In United States Patent No. 5,939,516 there is proposed production of a modified polyethylene terephthalate by incorporating in the polymer molecule a polyhydroxyl chain branching agent such as trimethylol propane, mesoerythritol, duclitol (galacticol), adonitol (ribitol), or pentaerythritol.

Addition of a polyamide to reduce the concentration of acetaldehyde in bottles made from polyethylene terephthalate is taught in United States Patents Nos. 5,340,884, 5,650,469, and 4,837,115.

Production of a copolyester by polycondensing

terephthalic acid, isophthalic acid and a glycol, followed by a two stage heat treatment to reduce the acetaldehyde content is proposed in United States Patent No. 5,864,005.

Use of primary and secondary antioxidants to reduce the amount of acetaldehyde generated by subjecting polyethylene terephthalate to high temperatures is taught in United States Patent No. 5,874,517. Addition of primary and secondary antioxidants to reduce gel formation in polyethylene terephthalate is suggested in United States Patent No. 5,874,515.

United States Patent No. 5,863,964 proposes addition of dl-α-tocopherol to a liner component for a potable fluid container for preventing off-flavours due to the presence of aldehydes in the fluid.

A stabilising system is proposed in United States Patent No. 5,844,027 for organic material susceptible to thermal, oxidative or/and light induced deterioration. This includes α-tocopherol.

There is a need to provide a polymer additive for incorporation in moulding compositions which comprise polyethylene terephthalate, a copolyester thereof, or a blend of one of these with a polyamide, in order to reduce the amount of acetaldehyde formed during processing of such moulding compositions.

There is a further need to provide a polymer additive which does not lead to discolouration or haze when polyester moulding compositions which consist of or contain polyethylene terephthalate or a copolymer thereof and which contain the polymer additive are subjected to injection moulding and/or blow moulding.

There is a still further need to provide a process for production from moulding compositions containing polyethylene terephthalate of blow moulded articles, such as bottles and preforms therefor, which will not release significant quantities of acetaldehyde after formation.

It is an object of the present invention to reduce residual aldehyde levels in polyester materials without the

occurrence of discolouration of the material during the injection moulding process.

According to the present invention there is provided a polymer additive for addition to a thermoplastic moulding composition comprising polyethylene terephthalate or a copolyester thereof so as to effect reduction of the level of acetaldehyde resulting after processing thereof, said polymer additive comprising a hydroxylic compound selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy groups, and cycloaliphatic hydoroxylic compounds containing at least two hydroxy groups.

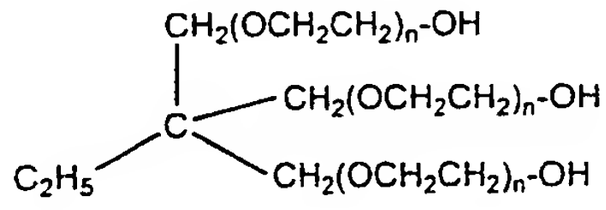
Any aliphatic chain in the hydroxylic compound can include not only carbon atoms but also one or more hetero atoms which may be selected, for example, from nitrogen, oxygen and sulphur atoms. Any cycloaliphatic ring present in the hydroxylic compound can be monocyclic or part of a bicyclic or polycyclic ring system and may be carbocyclic or heterocyclic. Any heterocyclic ring present in the hydroxylic compound can be monocyclic or part of a bicyclic or polycyclic ring system and may include one or more hetero atoms which may be selected, for example, from nitrogen, oxygen and sulphur atoms.

The hydroxylic compounds preferably contain from 3 to about 8 hydroxy groups. They may contain one or more substituents, such as ether, carboxylic acid, carboxylic acid amide or carboxylic acid ester groups.

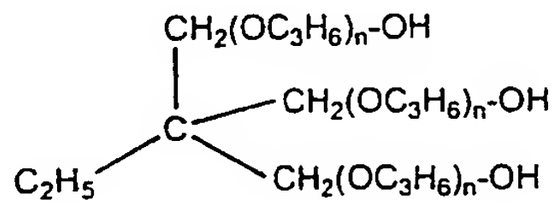
Preferred hydroxylic compounds include those having a pair of hydroxy groups which are attached to respective carbon atoms which are separated one from another by at least one atom. Especially preferred hydroxylic compounds are those in which a pair of hydroxy groups are attached to respective carbon atoms which are separated one from another by a single carbon atom.

As examples of suitable hydroxylic compounds there can be mentioned diols such as ethylene glycol, propane-1,2-

diol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,2-diol, 2-methylpentane-2,4-diol, 2,5-dimethyl-hexane-2,5-diol, cyclohexane-1,2-diol, cyclohexane-1,1-dimethanol, diethylene glycol, triethylene glycol, and polyethylene glycols having, for example, a molecular weight from about 800 to about 2000, such as Carbowax™ 1000 which has a molecular weight of about 950 to about 1050 and contains from about 20 to about 24 ethyleneoxy groups per molecule; triols, such as glycerol, trimethylolpropane, 2,3-di-(2'-hydroxyethyl)-cyclohexan-1-ol, hexane-1,2,6-triol, 1,1,1-tris-(hydroxymethyl)ethane, 3-(2'-hydroxyethoxy)-propane-1,2-diol, 3-(2'-hydroxypropoxy)-propane-1,2-diol, 2-(2'-hydroxyethoxy)-hexane-1,2-diol, 6-(2'-hydroxypropoxy)-hexane-1,2-diol, 1,1,1-tris-[(2'-hydroxyethoxy)-methyl]-ethane, 1,1,1-tris-[(2'-hydroxypropoxy)-methyl]-propane, 1,1,1-tris-(4'-hydroxyphenyl)-ethane, 1,1,1-tris-(hydroxyphenyl)-propane, 1,1,3-tris-(dihydroxy-3-methylphenyl)-propane, 1,1,4-tris-(dihydroxyphenyl)-butane, 1,1,5-tris-(hydroxyphenyl)-3-methylpentane, trimethylolpropane ethoxylates of the formula:



in which n is an integer, or trimethylolpropane propoxylates of the formula:



in which n is an integer, for example a trimethylolpropane propoxylate which has a molecular weight of about 1000; polyols such as pentaerythritol, dipentaerythritol, and tripentaerythritol; and saccharides, such as cyclodextrin, D-mannose, glucose, galactose, sucrose, fructose, xylose, arabinose, D-mannitol, D-sorbitol, D- or L-arabitol,

xylitol, iditol, talitol, allitol, altritol, guilitol, erythritol, threitol, and D-gulonic-γ-lactone; and the like. Mixtures of two or more such compounds can be used. Especially preferred are aliphatic hydroxylic compounds which contain from 3 to about 8 hydroxy groups.

The invention further provides a thermoplastic moulding composition comprising a polymer component comprising polyethylene terephthalate or a copolyester thereof and an amount effective to cause reduction of the level of acetaldehyde resulting after processing thereof of a hydroxylic compound uniformly distributed therein, said hydroxylic compound being selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy groups, and cycloaliphatic hydroxylic compounds containing at least two hydroxy groups.

Also provided in accordance with the present invention is a process for the production of a moulded article which comprises providing a thermoplastic moulding composition comprising a polymer component comprising polyethylene terephthalate or a copolyester thereof having an amount effective to cause reduction of the level of acetaldehyde resulting after processing thereof of a hydroxylic compound uniformly distributed therein, said hydroxylic compound being selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy groups, and cycloaliphatic hydroxylic compounds containing at least two hydroxy groups, and subjecting said thermoplastic moulding composition to an injection moulding step thereby to form a moulded article. Such a moulded article can be a preform for use in a subsequent blow moulding step to form a bottle.

The invention also provides the use of a hydroxylic compound selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy

groups, and cycloaliphatic hydroxylic compounds containing at least two hydroxy groups as an additive to a thermoplastic moulding composition comprising a polymer component comprising polyethylene terephthalate or a copolyester thereof for the reduction of the amount of acetaldehyde formed upon subjecting said moulding composition to melt processing.

By following the teachings of the invention it is possible to produce a thermoplastic polyester material with excellent reduction in levels of aldehyde without producing any discolouration of the material upon processing thereof. Thus it is possible to produce preforms and bottles of excellent clarity and lack of haze or colour by injection moulding a polymer composition containing polyethylene terephthalate or a copolyester thereof, optionally in admixture with a polyamide, and a hydroxylic compound selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy groups, and cycloaliphatic hydroxylic compounds containing at least two hydroxy groups, so as to form a preform and thereafter blow moulding the resultant preform to form a bottle which exhibits a greatly reduced amount of free acetaldehyde compared with preforms and bottles which lack the added aliphatic hydroxylic compound.

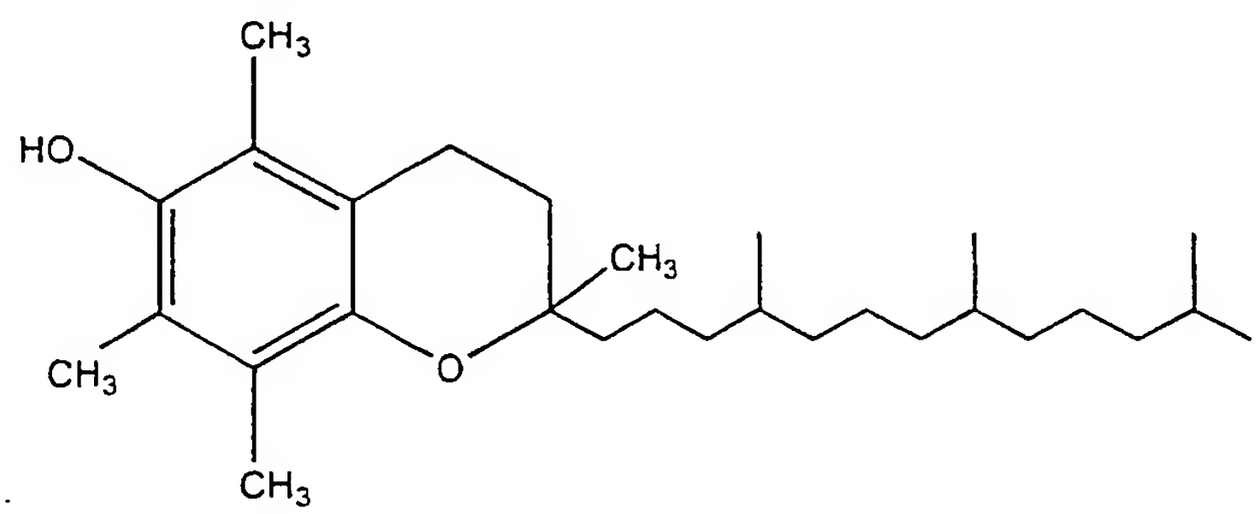
The hydroxylic compound can be used in combination with an antioxidant.

In view of the desire in the packaging industry for transparency in the finished polyethylene terephthalate articles, such as bottles, it is preferred to utilise antioxidants which do not tend to give rise to coloured reaction products. Thus, although amine antioxidants are widely used in the rubber industry, the fact that many of them tend to give rise to coloured products is not usually a problem because the rubber product is very often filled with a highly coloured filler, such as carbon black. However, amine antioxidants are generally not suitable for use in the

present invention since many of them tend to impart an unacceptable colour to any product in which they are incorporated due to the formation of coloured oxidation products.

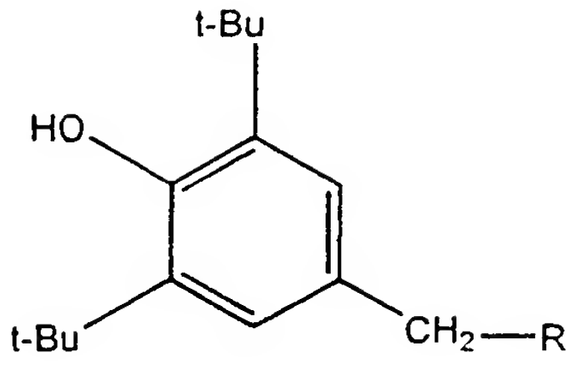
The antioxidant is preferably selected from hindered phenol antioxidants, phosphite antioxidants, phosphonate antioxidants, phosphonite antioxidants, phosphate antioxidants, and lactone antioxidants.

A preferred class of antioxidants for use in the present invention is hindered phenol antioxidants. Such compounds typically contain bulky groups, often tertiary alkyl groups or tertiary aralkyl groups, in the 2- and/or 6-positions of the phenol ring as well as often a 4-substituent. Amongst such antioxidants there can be mentioned 4-substituted-2,6-di-tertiary butyl phenols. A particularly preferred example of such an antioxidant is α-tocopherol, which has the formula:

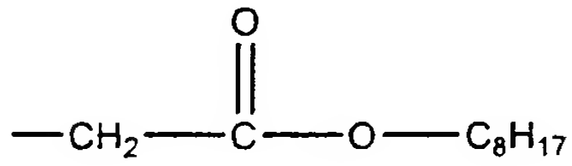


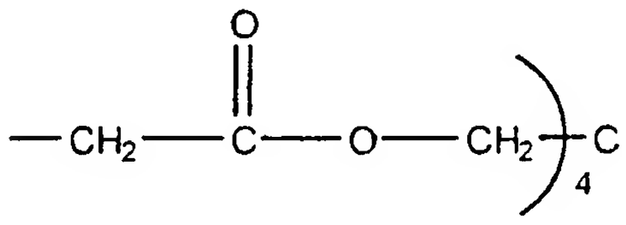
This compound occurs in nature and is known as Vitamin E. The naturally occurring compound has the R,R,R chiral configuration. It is, however, available in synthetic form as d,l-α-tocopherol. Preferably the synthetic form, d,l-α-tocopherol, is used. The synthetic form has 8 isomers each having a different chiral configuration.

Other hindered phenol antioxidants which can be considered for use in the present invention are those of the general formula:



in which R is hydrogen,





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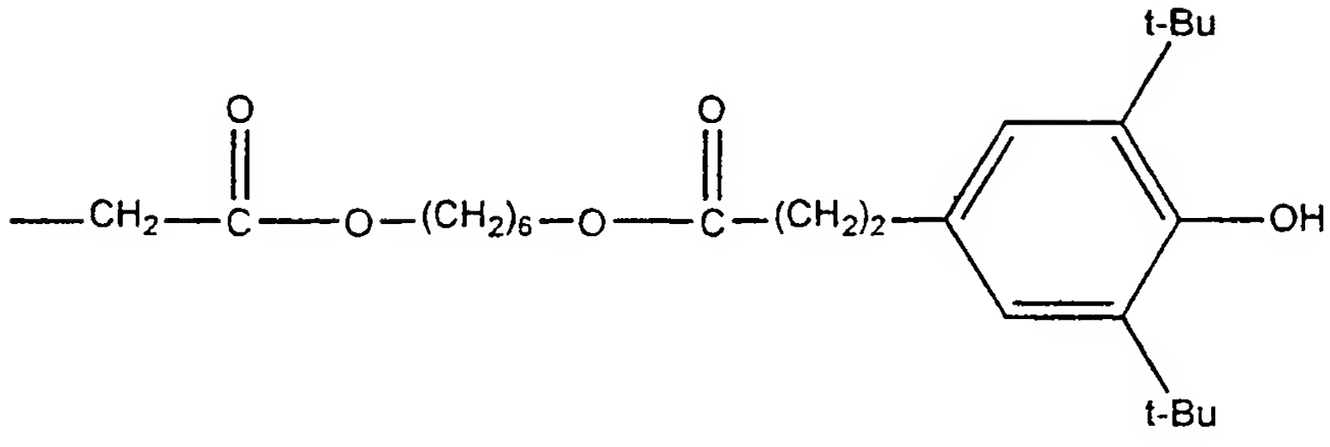
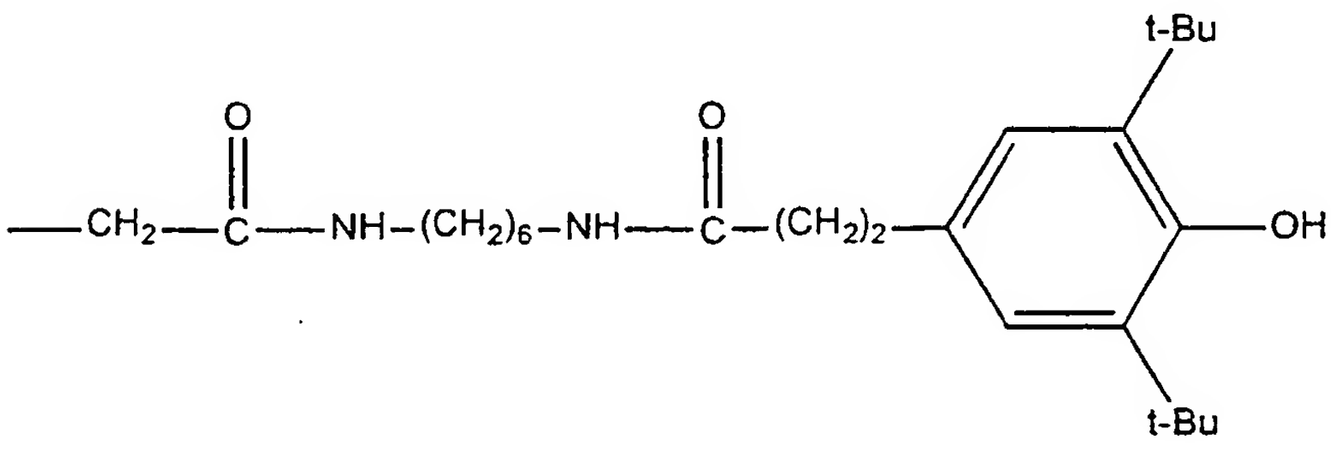
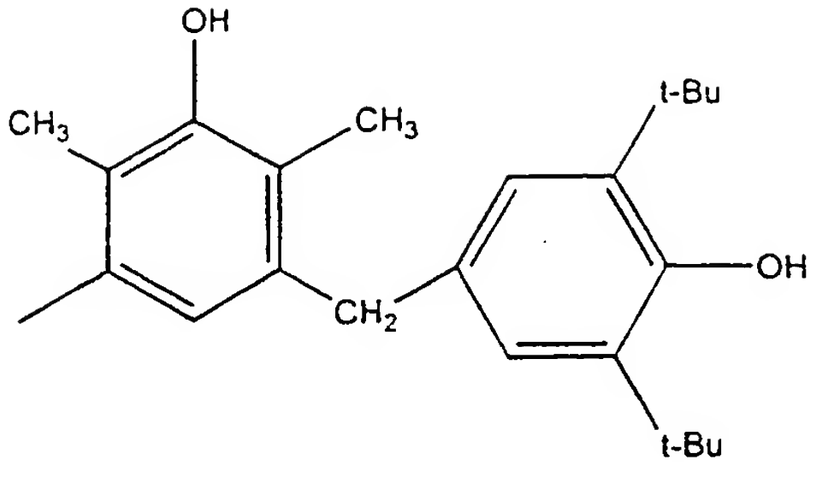
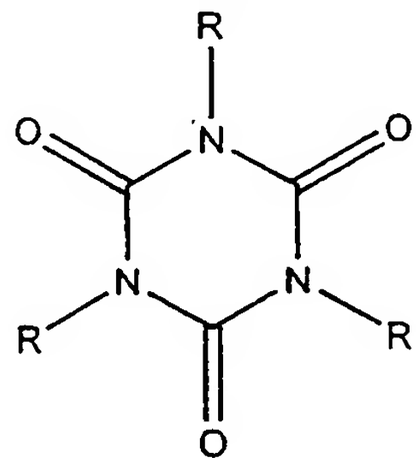




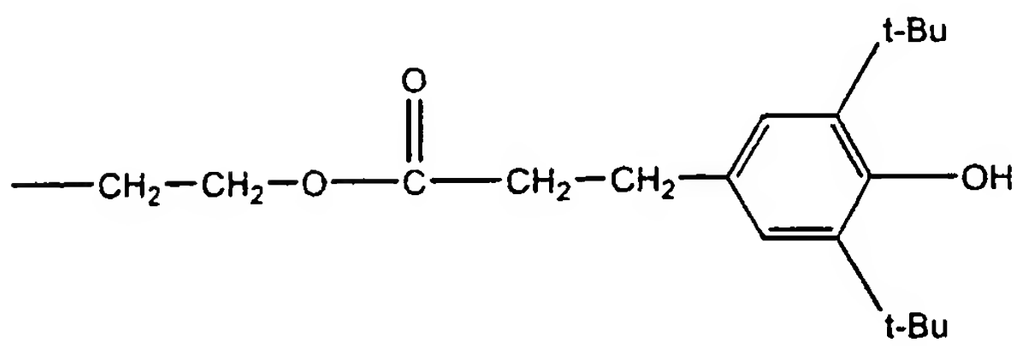
or



Other hindered phenol antioxidants include antioxidants containing an isocyanurate group of the formula:



where R is



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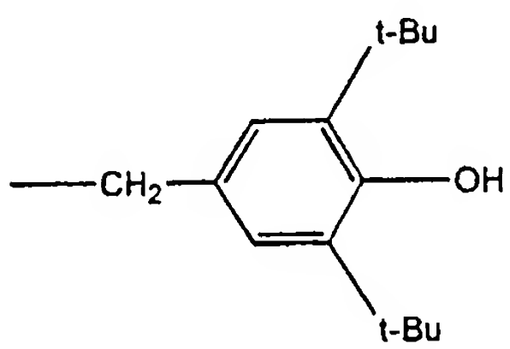
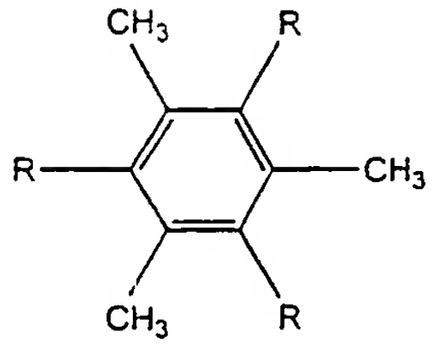
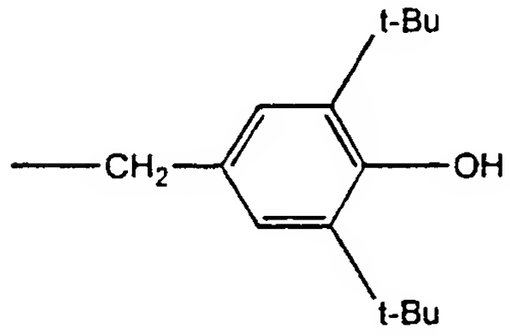


Another type of hindered phenol antioxidant which can be considered for use in the present invention is

exemplified by compounds of the formula:



in which R is



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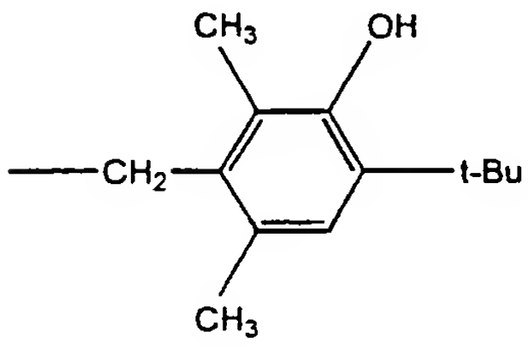
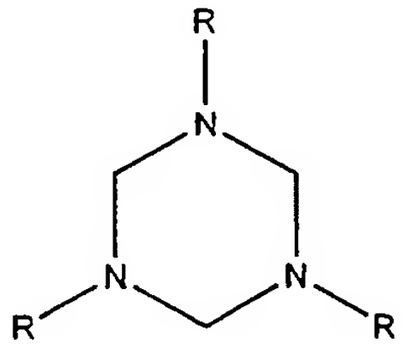
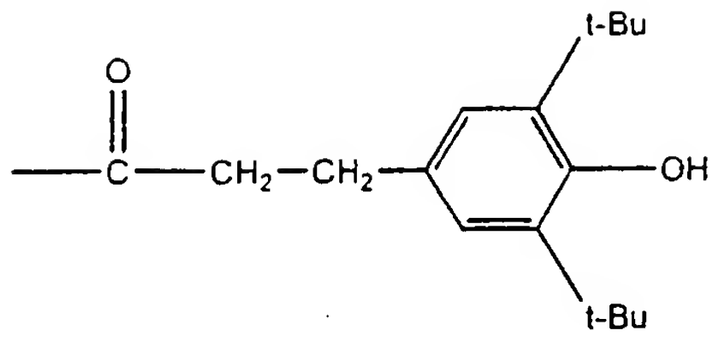


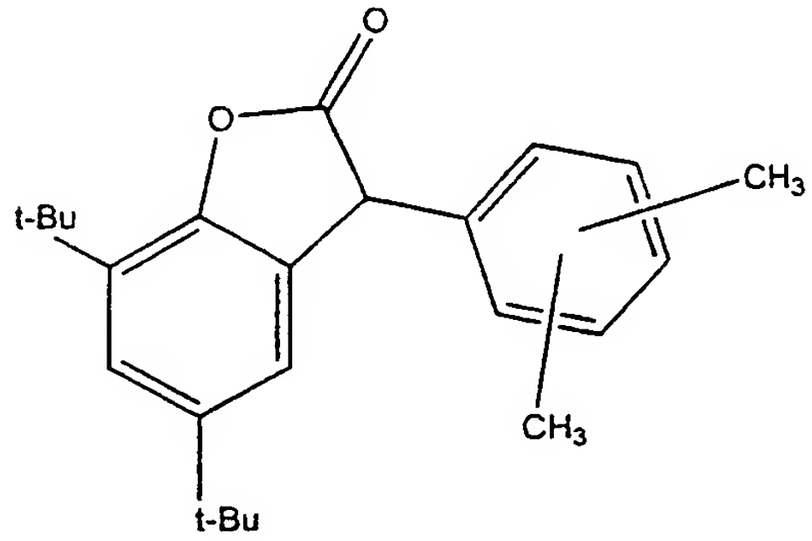
Yet another type of hindered phenol antioxidant is exemplified by the hexahydro-1,3,5-triazine compound of the formula:



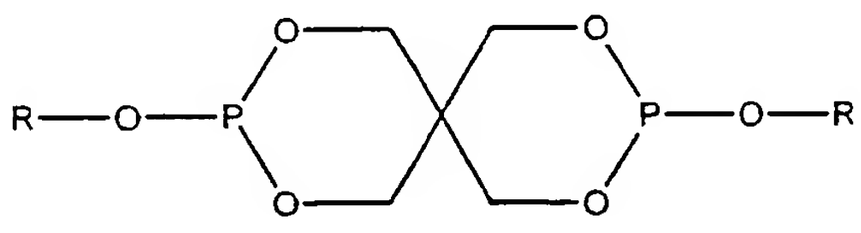
in which R represents a group of the formula:



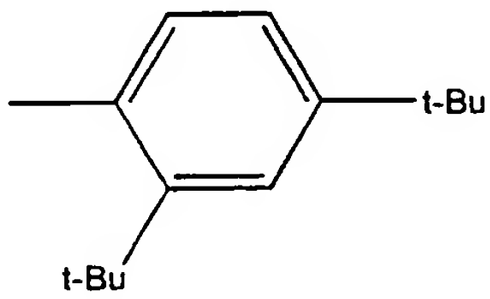
Lactone-based antioxidants can alternatively be used, for example, the antioxidant of the formula:

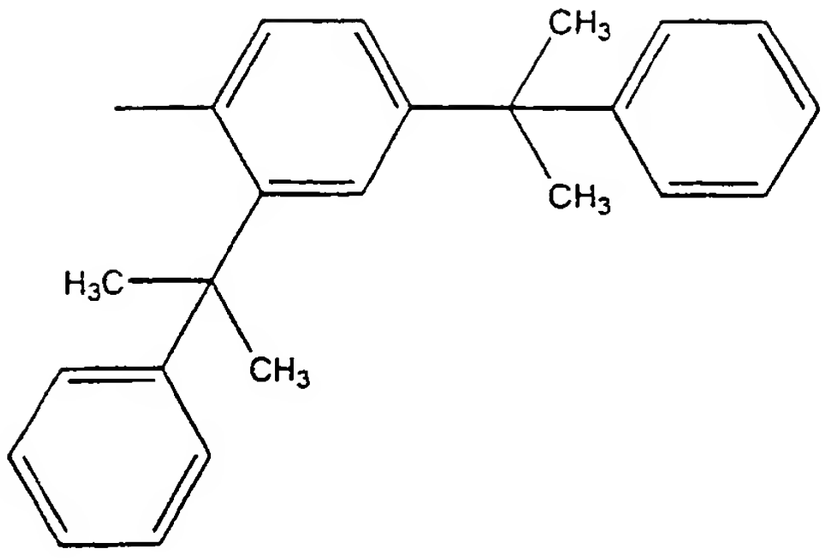


Phosphite antioxidants are another class of antioxidants that can be used, for example, those of the formula:



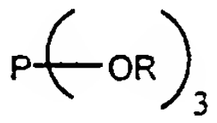
in which R is



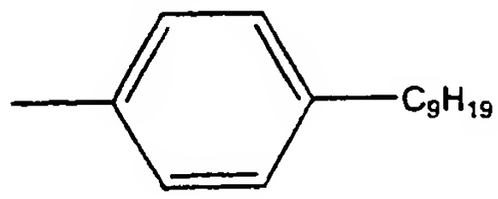


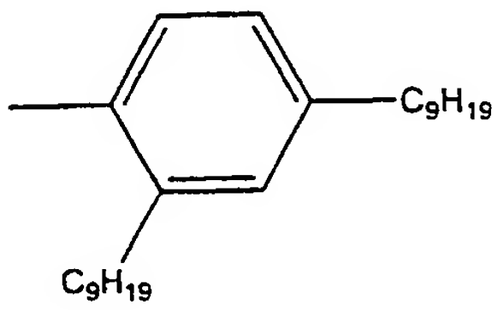
or $C_{18}H_{37}$.

Other phosphite antioxidants include those of the formula

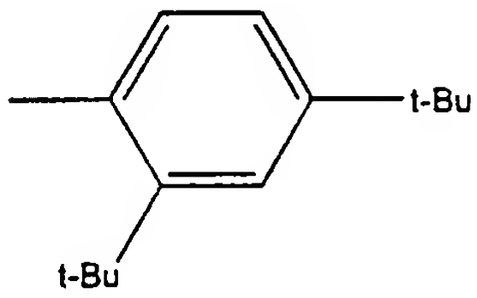


in which R represents a group of the formula:

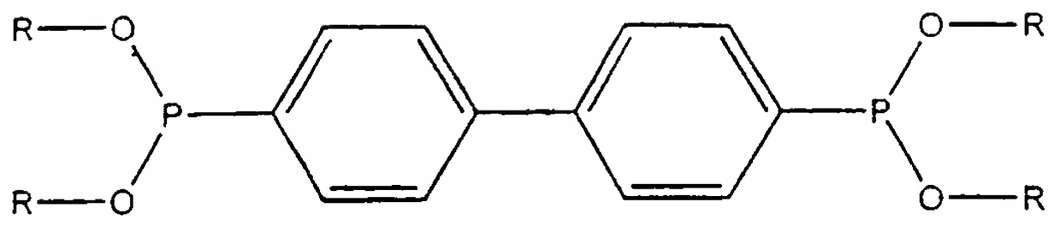




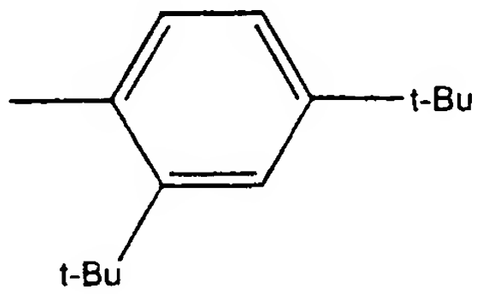
or



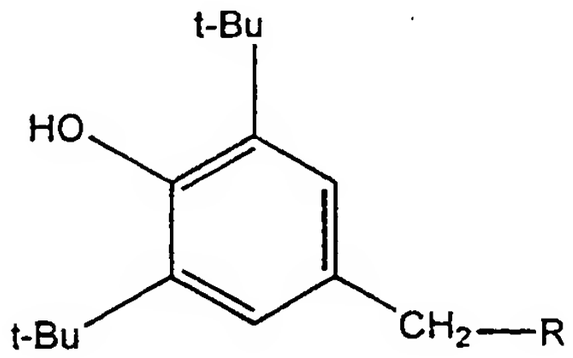
Also there can be mentioned phosphonate antioxidants of the formula:



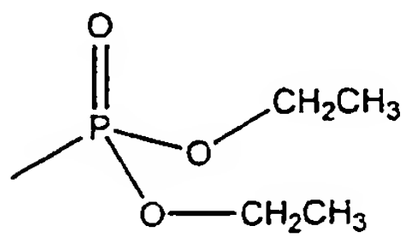
in which R represents a group of the formula:



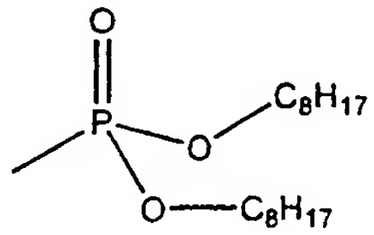
as well as those of the formula:



in which R represents a group of formula:



or



The advantage of using α-tocopherol is that, not only is it an extremely efficient antioxidant, but also it is non-toxic. Thus it is an extremely suitable material to use in a packaging material that is to be used for packaging bottled drinks and other foodstuffs.

A mixture of two or more antioxidants of the same or different type can be used, if desired. For example, it is possible to use a mixture of a hindered phenol type of

antioxidant and a phosphite type of antioxidant.

It is preferred that in the polymer additive of the invention the hydroxylic compound:liquid carrier weight ratio ranges from about 0.1:1 to about 3:1. Preferably this ratio is from about 0.5:1 to about 1.5:1.

The amount of hydroxylic compound to be used in the thermoplastic moulding composition can vary within wide limits but typically ranges from about 0.0001 % by weight up to about 2 % by weight based upon the weight of the polymer component, i.e. the polyester or copolyester or blend thereof with a polyamide. More preferably the amount of hydroxylic compound used ranges from about 0.01 % by weight up to about 1 % by weight based upon the polymer component.

The amount of antioxidant or mixture of antioxidants, when used in the thermoplastic moulding composition, can vary within wide limits but typically ranges from about 0.0001 % by weight up to about 2 % by weight based upon the weight of the polymer component, i.e. the polyester or copolyester or blend thereof with a polyamide. More preferably, the amount of antioxidant or antioxidant mixture used ranges from about 0.01 % by weight up to about 1 % by weight based upon the polymer component.

The polymer additive composition of the invention preferably includes a polymer-compatible organic liquid carrier. Such a carrier must be compatible with the polyethylene terephthalate or copolyester thereof and with the other components to be included in the thermoplastic moulding composition of the invention. Typical carriers includes hydrocarbons, hydrocarbon mixtures, alcohols, esters and mixtures of two or more thereof.

Preferably the polyester-compatible organic liquid carrier is an oil-based vehicle. Examples of such vehicles are the materials sold as Clearslip™ 2 and Clearslip™ 3 by ColorMatrix Europe Ltd, of Units 9-11 Unity Grove, Knowsley Business Park, Merseyside, L34 9GT.

It is preferred that in the polymer additive of the invention the antioxidant:liquid carrier weight ratio ranges

from about 0.1:1 to about 3:1. Preferably this ratio is from about 0.5:1 to about 1.5:1.

In practising the invention it is possible to incorporate in the additive at least one polyester-compatible colorant.

Although it will normally be convenient to incorporate the hydroxylic compound and the optional ingredients, including any antioxidant and any colorant, into the thermoplastic moulding composition of the invention in the form of the polymer additive of the invention, it is alternatively possible, under appropriate conditions to add these components to the polyethylene terephthalate, copolyester thereof, or admixture with a polyamide, in undiluted form. In this case no organic liquid carrier is used.

The invention is further illustrated in the following Examples in which all parts are by weight, unless otherwise specified.

Examples 1 to 11

A series of polymer additive mixtures was made up by mixing the ingredients listed in Table 1 in the ratio of the listed amounts. Each mixture was then used in conjunction with the specified weight of a granular polyethylene terephthalate (PET) moulding composition to form bottle preforms with a weight of 46.9 g. A comparison preform was prepared on the same occasion under identical conditions in each case, except that the additive mixture under test was omitted.

In each of Examples 1 to 11 the polyester was extruded in the presence of the additive mixture in an injection moulding machine having two cavities using a mould temperature of 283°C, a barrel temperature of 278°C at the nozzle end and 275°C in the rest of the barrel, an injection pressure of 100 bar and a cycle time of 38.5 s.

The acetaldehyde content of the resulting preforms was determined by the liquid/gas headspace chromatography technique described by F. Villain *et al.*, Journal of Polymer Science, Vol. 52, 55-60 (1994).

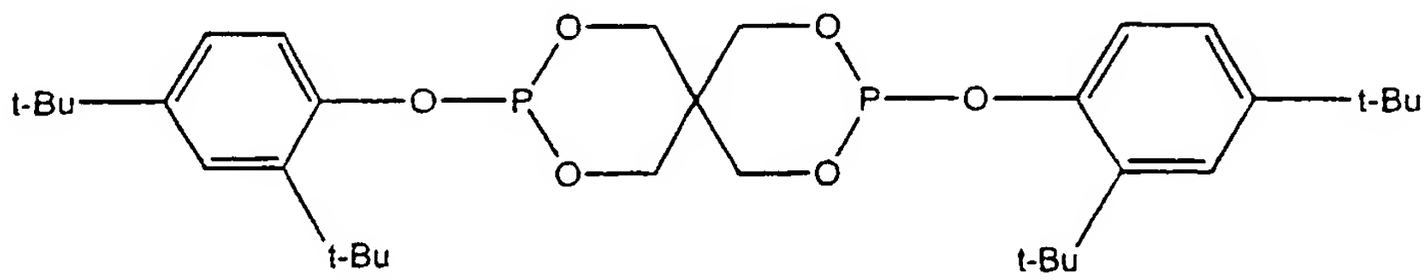
The results are set out in Table 1.

TABLE 1

Example No.	Trimethylolpropane	Vitamin E	U-626	Clearslip™ 2	Parts of PET	% reduction of CH_3CHO
1	0.27	0.10	0.00	0.15	99.58	65
2	0.20	0.17	0.00	0.00	99.63	62
3	0.20	0.10	0.20	0.00	99.50	59
4	0.20	0.10	0.20	0.25	99.25	63
5	0.20	0.17	0.00	0.00	99.63	59
6	0.27	0.00	0.00	0.00	99.73	59
7	0.34	0.00	0.00	0.18	99.48	59
8	0.28	0.10	0.00	0.15	99.52	62
9	0.22	0.17	0.00	0.10	99.51	62
10	0.39	0.17	0.00	0.13	99.31	62
11	0.35	0.17	0.00	0.00	99.48	66

Notes:

1. U-626 is a bis-phosphite of pentaerythritol having the formula:



2. Clearslip™ 2 is an oil-based carrier available from ColorMatrix Europe Ltd, of Units 9-11 Unity Grove, Knowsley Business Park, Merseyside, L34 9GT.

Examples 12 and 13

The same general procedure was followed in these Examples as in Examples 1 to 11, except that trimethylol-propane was replaced by dipentaerythritol (DPE) and tripentaerythritol (TPE) respectively. The results are set out below in Table 2.

TABLE 2

Example No.	Type	Amount	Vitamin E	Clearslip™ 2	Parts of PET	% reduction of CH_3CHO
12	DPE	0.32	0.10	0.18	99.50	66
13	TPE	0.28	0.10	0.18	99.44	66

Examples 14 to 16

The same general procedure was followed as in Examples 1 to 11, except that the bottle preforms weighing 28 g each were extruded using a commercial injection moulding machine having 48 cavities. The injection pressure was 100 bar, while the barrel temperature ranged from 295°C at its nozzle end to 285°C at its inlet end, with intermediate parts of the barrel being at 279°C. The results are set out below in Table 3. Examples 14 and 15 used Clearslip™ 2 while Example 16 used Clearslip™ 3.

TABLE 3

Example No.	Trimethylolpropane	Vitamin E	Clearslip™	Parts of PET	% reduction of CH_3CHO
14	0.12	0.045	0.135	99.835	50
15	0.20	0.075	0.225	99.50	59
16	0.135	0.00	0.165	99.50	29

Examples 17 to 20

In these Examples various commercial injection moulding machines were used to make bottle preforms under conditions similar to those described above in relation to Examples 14 to 16. The results are summarised in Table 4 below.

TABLE 4

Example	Additive wt%	Additive components						
		Vitamin E wt%	TMP wt%	DPE wt%	TPE wt%	Clearslip 2	Clearslip 3	% reduction of CH_3CHO
17	0.2	-	-	0.1	-	-	0.1	37
18	0.3	-	-	0.15	-	-	0.15	46
19	0.5	-	-	0.25	-	-	0.25	55
20	0.2	-	-	-	0.1	-	0.1	40

Examples 21 to 35

In these Examples the same general procedure was used as was used in Examples 1 to 11.

The results are set out below in Table 5.

TABLE 5

Example	Additive wt%	Vitamin E wt%	TMP wt%	DPE wt%	TPE wt%	Clearslip™ 2	Clearslip™ 3	% reduction of CH_3CHO
21	0.3	0.015	0.143	-	-	0.143	-	61
22	0.5	0.025	0.238	-	-	0.238	-	67
23	0.7	0.035	0.333	-	-	0.333	-	64
24	0.3	0.015	0.150	-	-	0.135	-	64
25	0.5	0.225	0.250	-	-	0.225	-	67
26	0.3	0.015	-	-	0.165	0.120	-	70
27	0.5	0.025	-	-	0.275	0.200	-	64
28	0.3	-	0.15	-	-	0.15	-	42
29	0.5	-	0.25	-	-	0.25	-	58
30	0.7	-	0.35	-	-	0.35	-	58
31	0.3	-	-	0.15	-	0.15	-	52
32	0.5	-	-	0.25	-	0.25	-	64
33	0.7	-	-	0.35	-	0.35	-	61
34	0.3	-	-	-	0.165	0.135	-	58
35	0.5	-	-	-	0.275	0.225	-	64

Example 36

A coloured additive was prepared by mixing the following ingredients:

53.50%	Clearslip™ 2
40.00%	dipentaerythritol
1.00%	dl-α-tocopherol
1.50%	Solvent Blue 104

This additive was incorporated in bottle preforms as described in Example 1 in an amount of 0.25% of the weight of the botle preform. Bottles were blow moulded from such preforms. Good results were obtained.

CLAIMS:

1. A polymer additive for addition to a thermoplastic moulding composition comprising polyethylene terephthalate or a copolyester thereof so as to effect reduction of the level of acetaldehyde resulting after processing thereof, said polymer additive comprising a hydroxylic compound selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy groups, and cycloaliphatic hydoroxylic compounds containing at least two hydroxy groups, uniformly distributed in a polyester-compatible organic liquid carrier.

2. A polymer additive according to claim 1, in which in the hydroxyl compound contains a pair of hydroxy groups attached to respective carbon atoms which are separated one from another by a single carbon atom.

3. A polymer additive according to claim 1 or claim 2, in which said hydroxylic compound is selected from triglycerin, trimethylolpropane, dipentaerythritol, tripentaerythritol, D-mannitol, D-sorbitol, and xylitol.

4. A polymer additive according to any one of claims 1 to 3, in which the hydroxylic compound:liquid carrier weight ratio ranges from about 0.1:1 to about 1.5:1.

5. A polymer additive according to any one of claims 1 to 4, in which the polyester-compatible organic liquid carrier is an oil-based vehicle.

6. A polymer additive according to any one of claims 1 to 5, further comprising at least one polyester-compatible colorant.

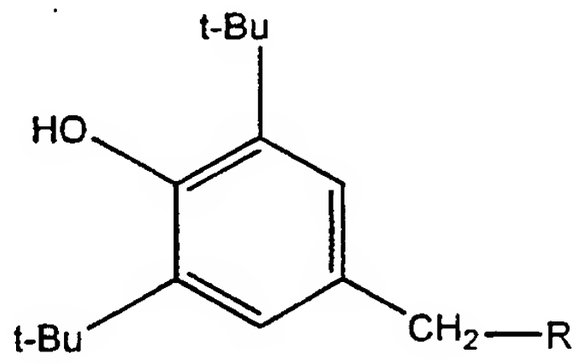
7. A polymer additive according to any one of claims 1 to

6, further comprising an antioxidant.

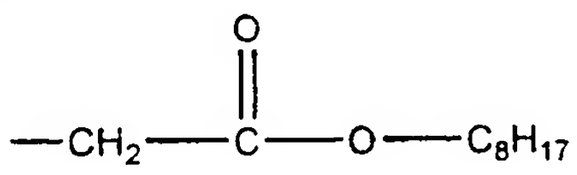
8. A polymer additive according to any one of claims 1 to 7, in which the antioxidant is a hindered phenol antioxidant.

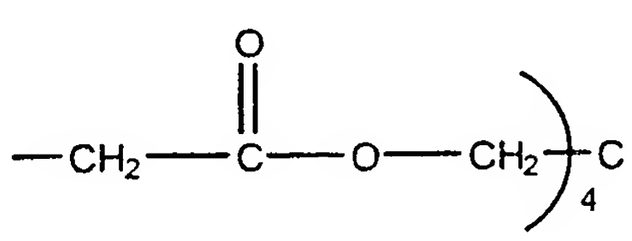
9. A polymer additive according to claim 8, in which the antioxidant is a 4-substituted-2,6-di-tertiary butyl phenol or an α-tocopherol.

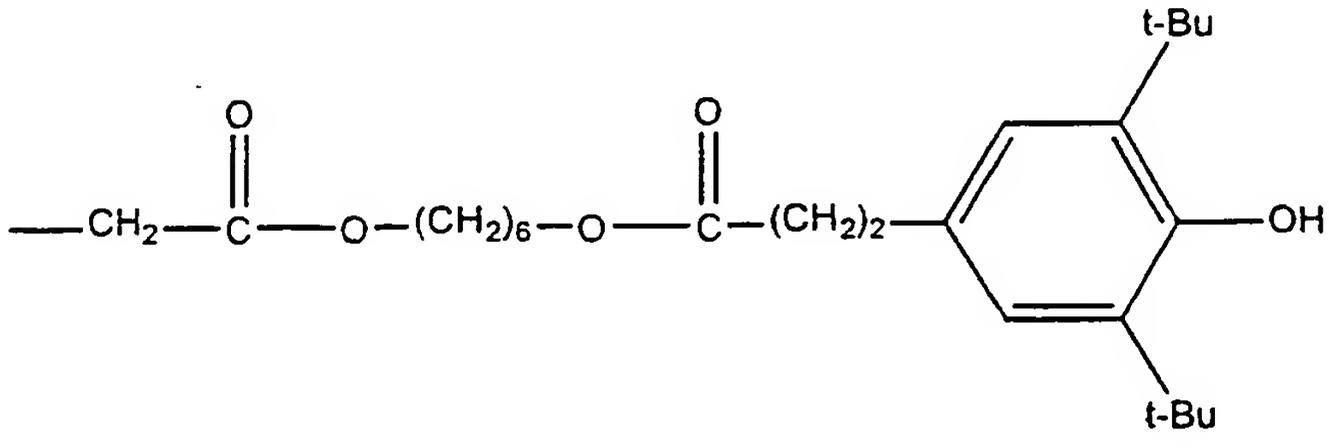
10. A polymer additive according to claim 10, in which the antioxidant has the formula:

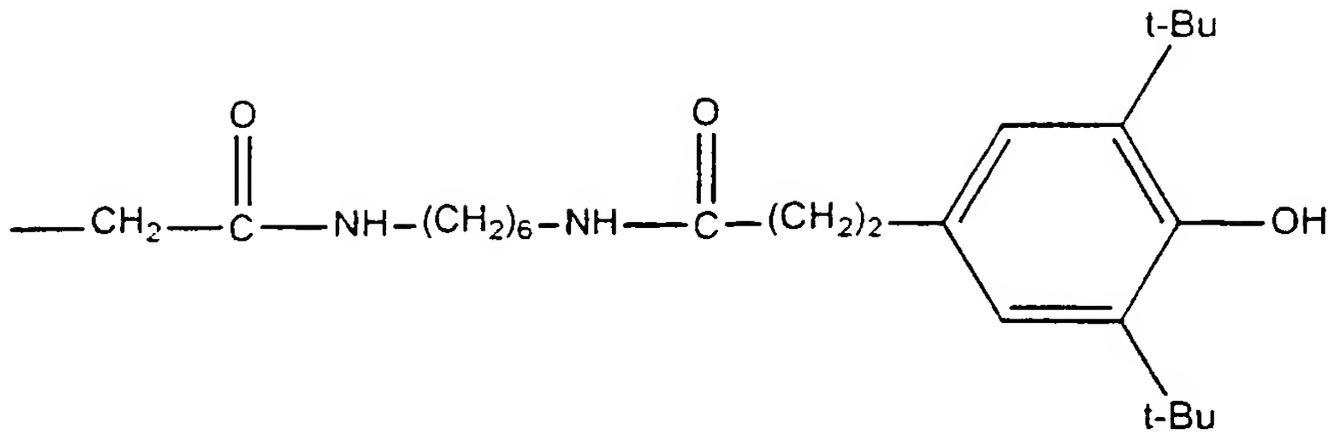


in which R is hydrogen,









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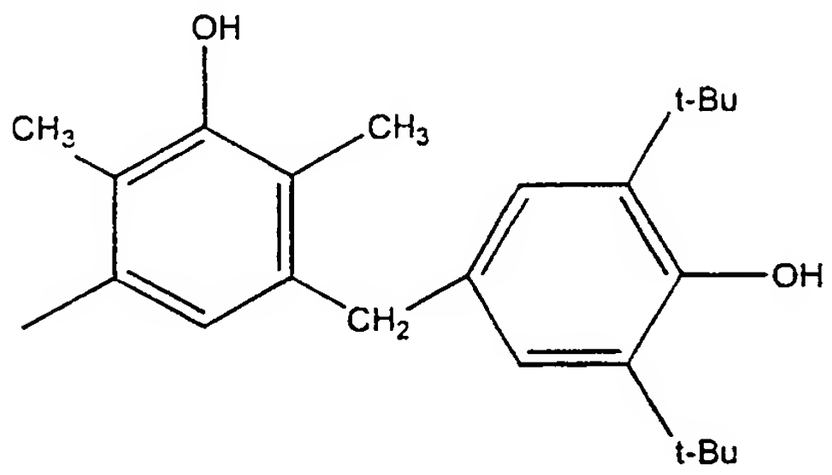
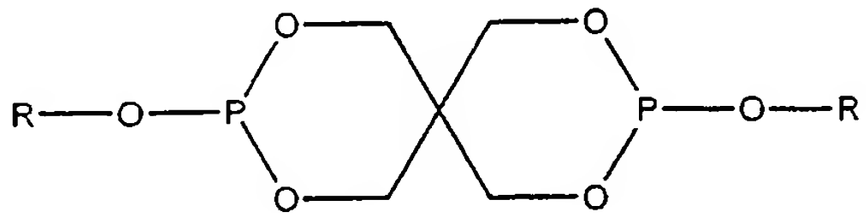


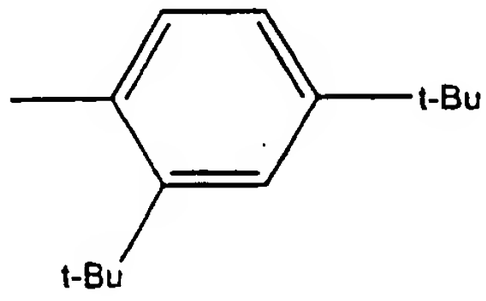
11. A polymer additive according to claim 9, in which the antioxidant comprises synthetic Vitamin E.

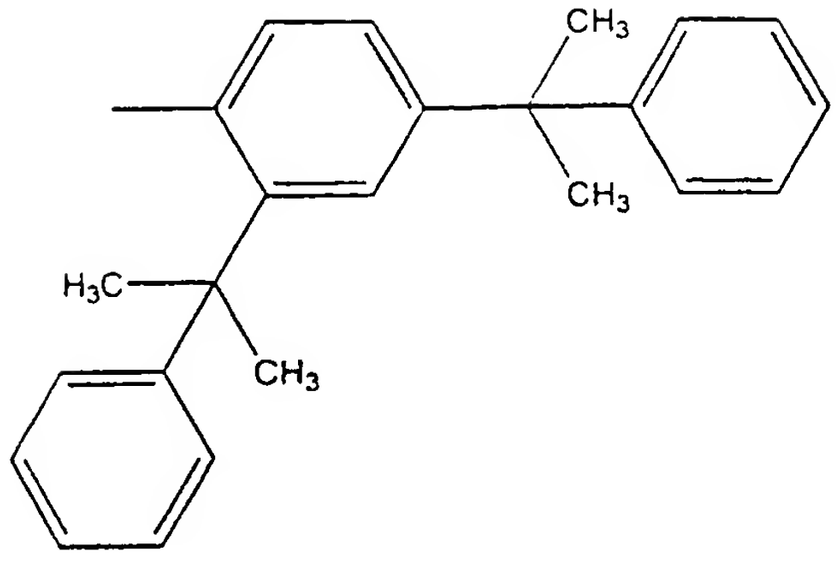
12. A polymer additive according to any one of claims 1 to 12, further comprising a phosphite antioxidant.

13. A polymer additive according to claim 12, in which the phosphite antioxidant has the structure:



in which R is





or $C_{18}H_{37}$.

14. A polymer additive according to any one of claims 1 to 13, in which the antioxidant:liquid carrier weight ratio ranges from about 0.1:1 to about 1.5:1.

15. A thermoplastic moulding composition comprising a polymer component comprising polyethylene terephthalate or a copolyester thereof and an amount effective to cause reduction of the level of acetaldehyde resulting after processing thereof of a hydroxylic compound uniformly distributed therein, said hydroxylic compound being selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy groups, and cycloaliphatic hydoroxylic compounds containing at least two hydroxy groups.

16. A thermoplastic moulding composition according to claim 15, in which the amount of said hydroxylic compound ranges from about 0.0001 % by weight up to about 2 % by weight based upon the weight of the polymer component.

17. A thermoplastic moulding composition according to claim 15 or claim 16, in which the hydroxylic compound contains a pair of hydroxy groups attached to respective carbon atoms

which are separated one from another by a single carbon atom.

18. A thermoplastic moulding composition according to any one of claims 15 to 17, in which said hydroxylic compound is selected from triglycerin, trimethylolpropane, dipentaerythritol, tripentaerythritol, D-mannitol, D-sorbitol, and xylitol.

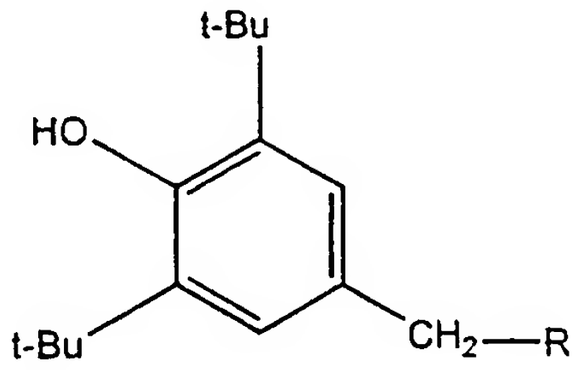
19. A thermoplastic moulding composition according to any one of claims 15 to 18, further comprising an antioxidant.

20. A thermoplastic moulding composition according to any one of claims 15 to 18, in which the amount of antioxidant compound ranges from about 0.0001 % by weight up to about 2 % by weight based upon the weight of the polymer component.

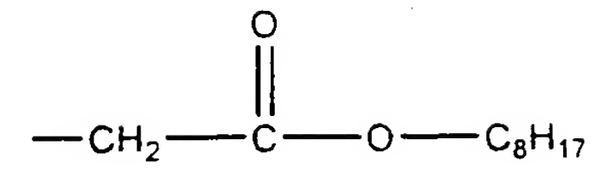
21. A thermoplastic moulding composition according to claim 19 or claim 20, in which the antioxidant is a hindered phenol antioxidant.

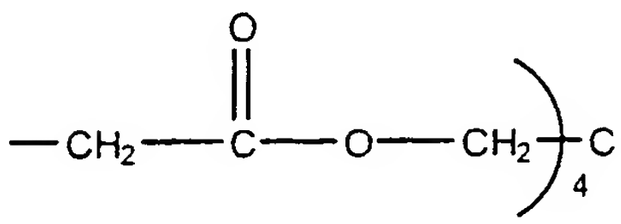
22. A thermoplastic moulding composition according to claim 21, in which the antioxidant is a 4-substituted-2,6-di-tertiary butyl phenol or an α-tocopherol.

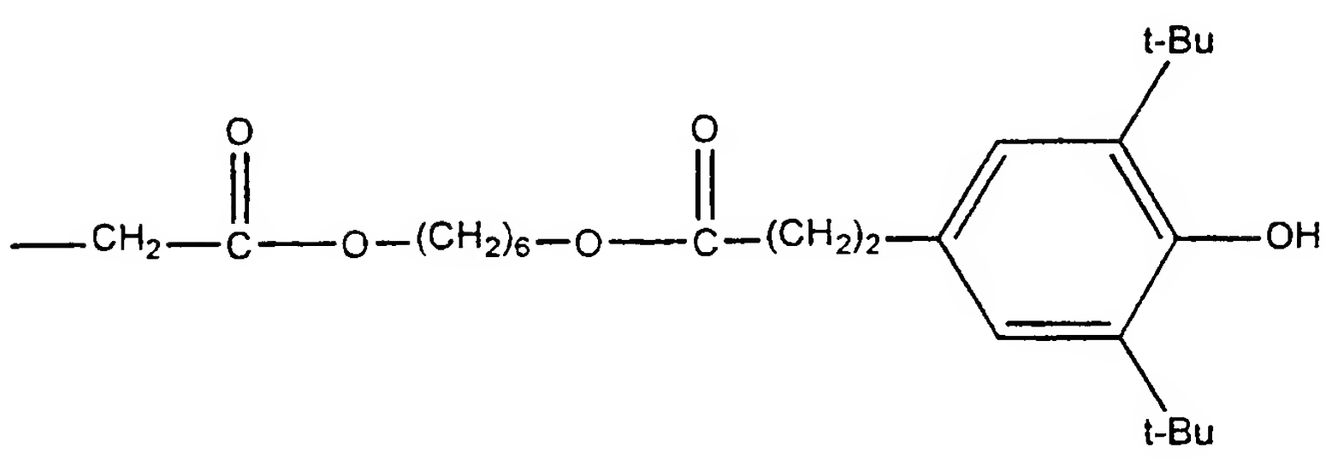
23. A thermoplastic moulding composition according to claim 22, in which the antioxidant has the formula:

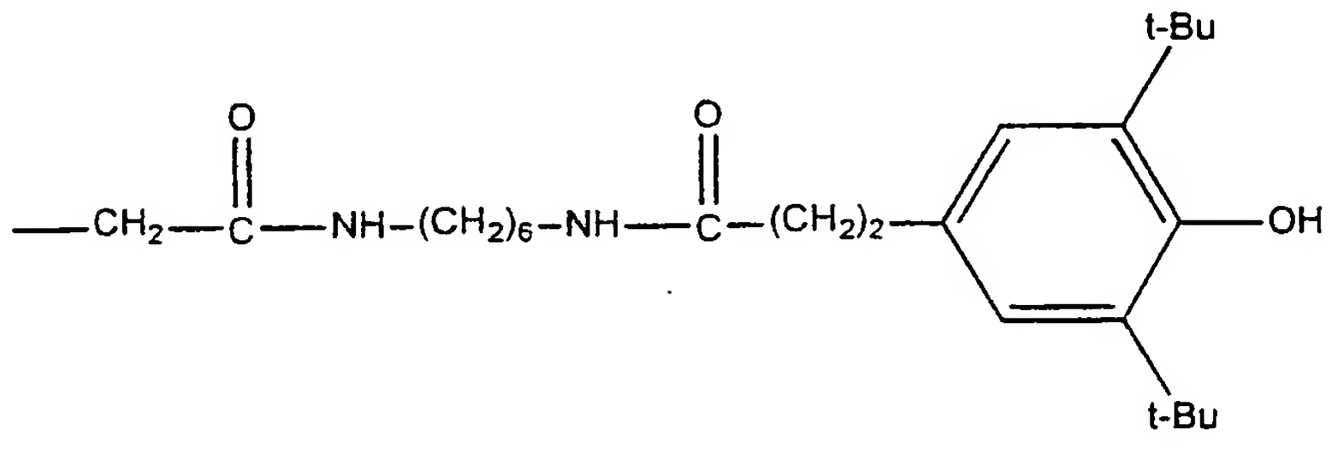


in which R is hydrogen,

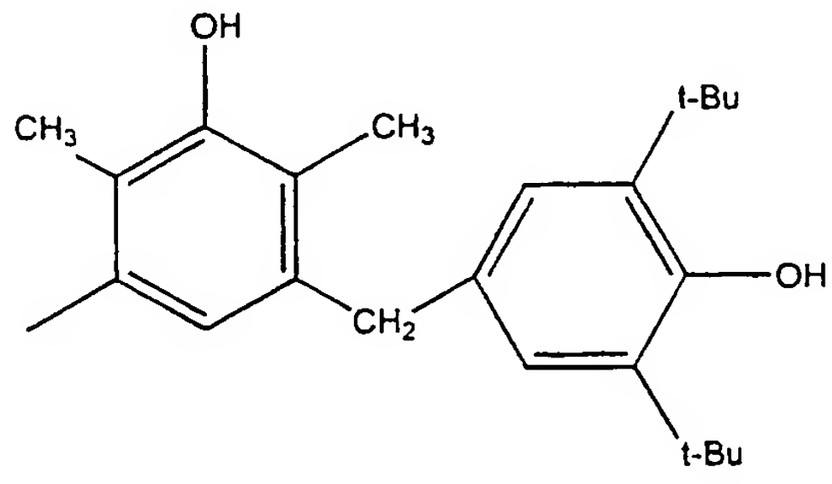








or

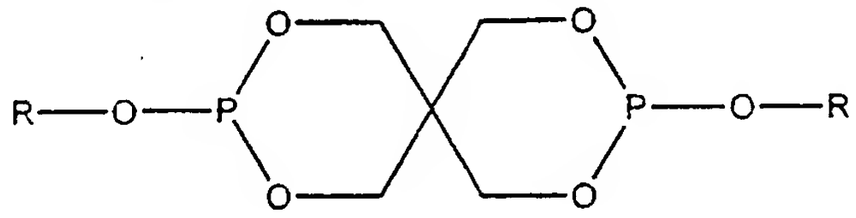


24. A thermoplastic moulding composition according to claim

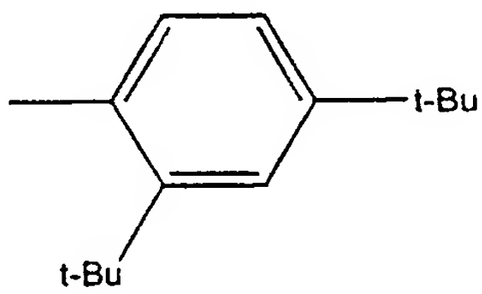
22, in which the antioxidant comprises synthetic Vitamin E.

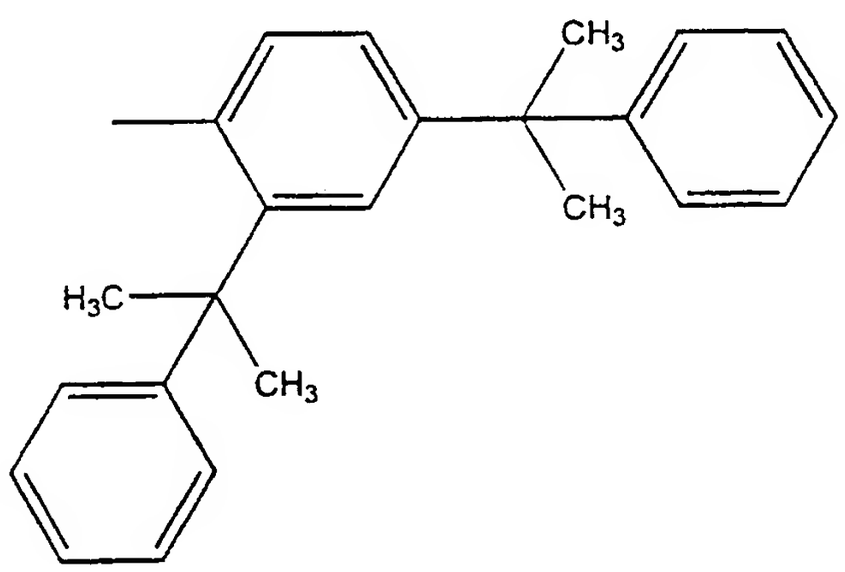
25. A thermoplastic moulding composition according to any one of claims 15 to 24, in which the antioxidant comprises a phosphite antioxidant.

26. A thermoplastic moulding composition according to claim 25, in which the phosphite antioxidant has the structure:



in which R is





or $C_{18}H_{37}$.

27. A thermoplastic moulding composition according to any one of claims 15 to 26, further comprising a minor amount of a liquid carrier for aliphatic hydroxylic compound.

28. A process for the production of a moulded article which

comprises providing a thermoplastic moulding composition comprising polyethylene terephthalate or a copolyester thereof having an amount effective to cause reduction of the level of acetaldehyde resulting after processing thereof of a hydroxylic compound uniformly distributed therein, said hydroxylic compound being selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy groups, and cycloaliphatic hydroxylic compounds containing at least two hydroxy groups, and subjecting said thermoplastic moulding composition to an injection moulding step thereby to form a moulded article.

29. A process according to claim 28, in which the moulded article is a preform for use in a subsequent blow moulding step to form a bottle.

30. A process according to claim 28 or claim 29, in which the hydroxylic compound contains a pair of hydroxy groups attached to respective carbon atoms which are separated one from another by a single carbon atom.

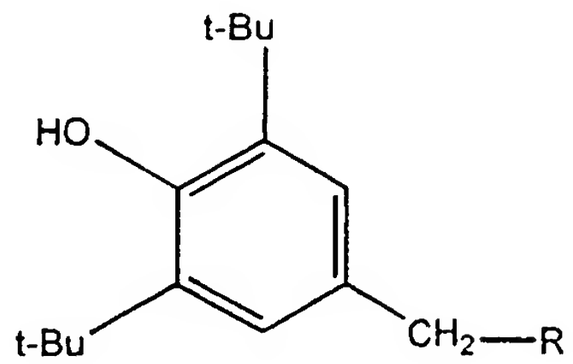
31. A process according to any one of claims 28 to 30, in which said hydroxylic compound is selected from triglycerin, trimethylolpropane, dipentaerythritol, tripentaerythritol, D-mannitol, D-sorbitol, and xylitol.

32. A process according to any one of claims 28 to 31, in which the thermoplastic moulding composition further comprises an antioxidant.

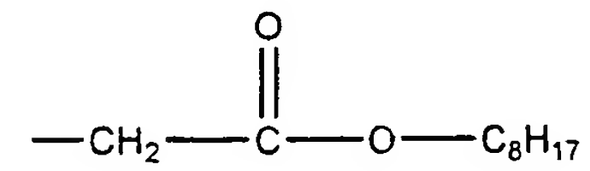
33. A process according to claim 32, in which the antioxidant is a hindered phenol antioxidant.

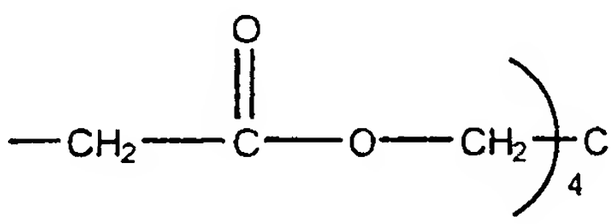
34. A process according to claim 33, in which the antioxidant is a 4-substituted-2,6-di-tertiary butyl phenol or an α-tocopherol.

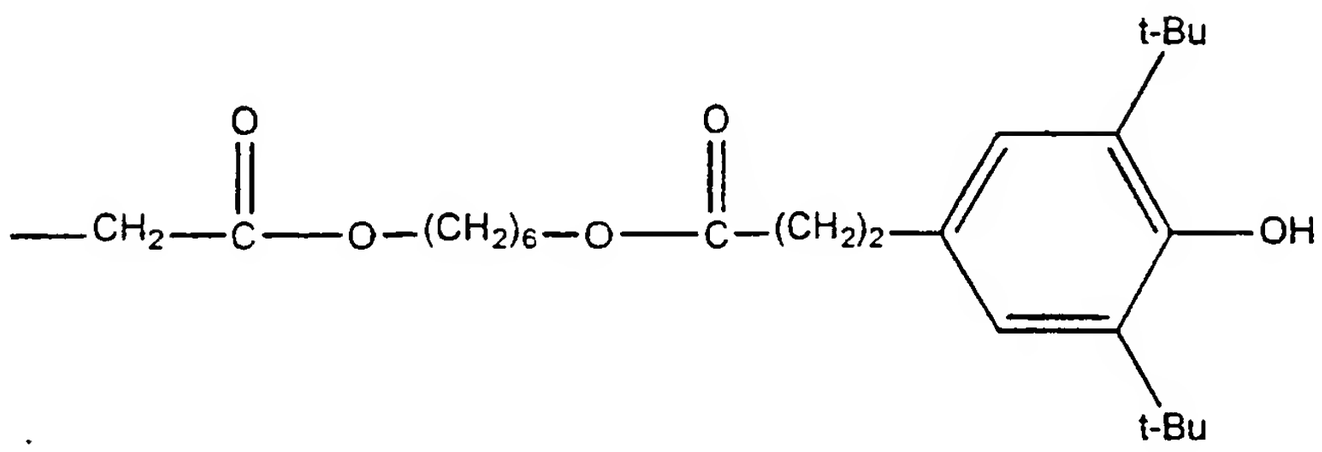
35. A process according to claim 33, in which the antioxidant has the formula:

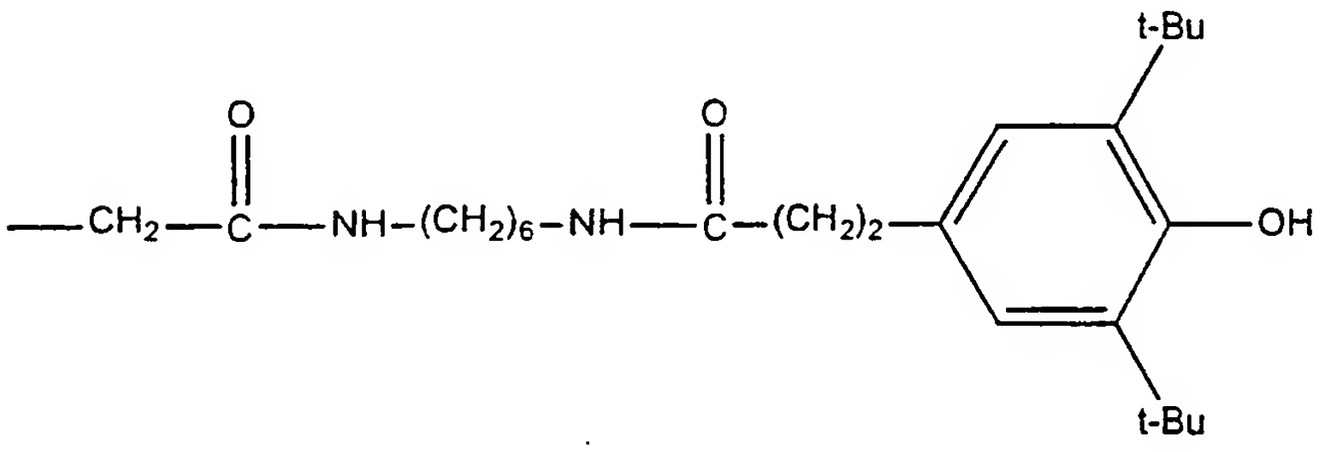


in which R is hydrogen,

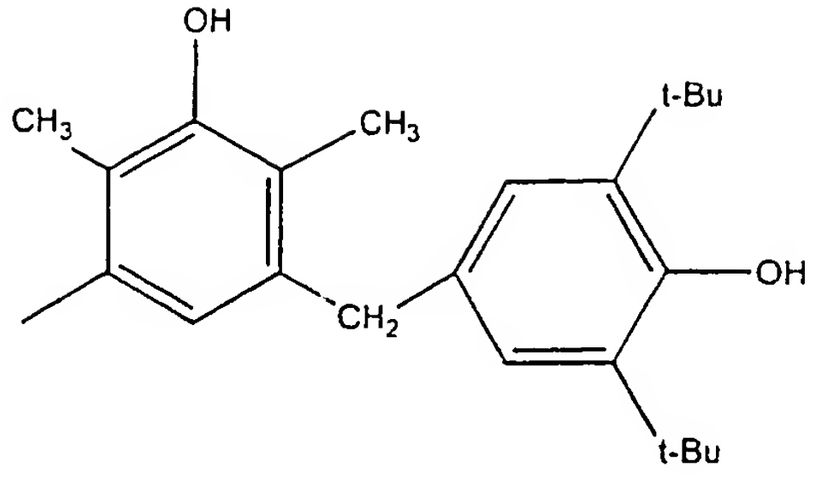








or



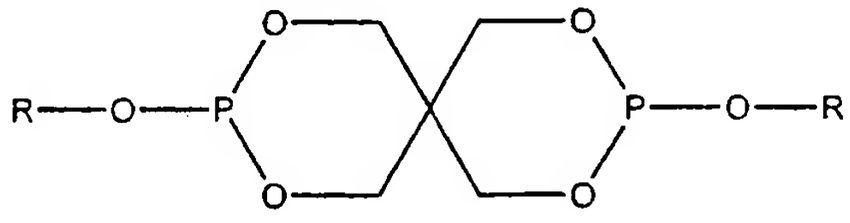
36. A process according to claim 34, in which the antioxidant comprises synthetic Vitamin E.

37. A process according to any one of claims 28 to 36, in which the thermoplastic moulding composition further comprises at least one polyester-compatible colorant.

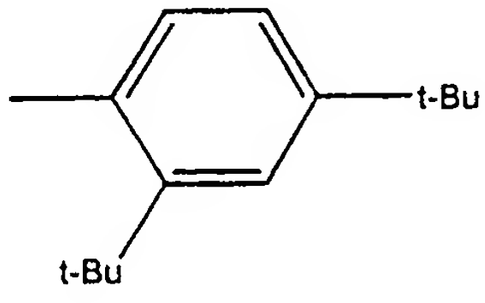
38. A process according to any one of claims 28 to 37, in which the thermoplastic moulding composition further comprises a minor amount of a liquid carrier for said aliphatic hydroxylic compound.

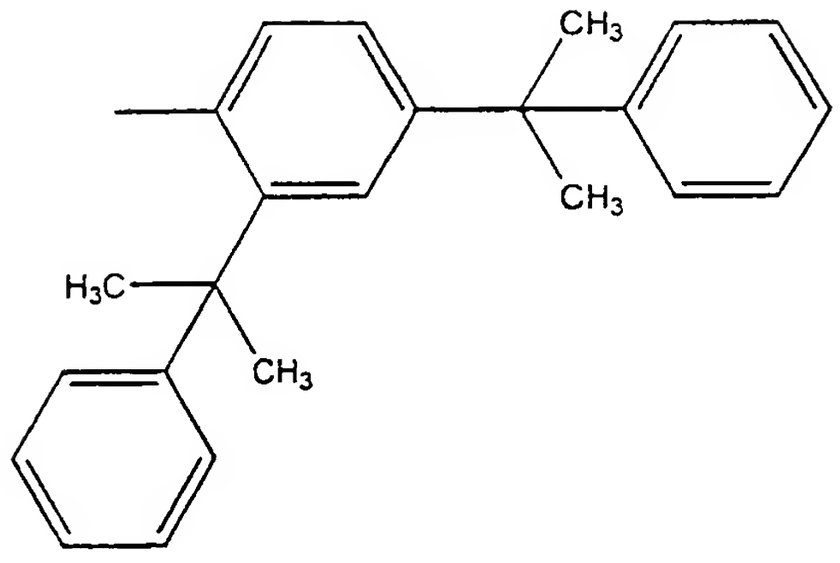
39. A process according to any one of claims 28 to 38, in which the antioxidant comprises a phosphite antioxidant.

40. A process according to claim 39, in which the phosphite antioxidant has the structure:



in which R is





or $C_{18}H_{37}$.

41. Moulded articles made by a process according to any one of claims 28 to 40.

42. Moulded articles according to claim 41, which are preforms for bottles.

43. Bottles blow moulded from a preform according to claim 42.

44. The use of a hydroxylic compound as an additive to a thermoplastic moulding composition comprising a polymer component comprising polyethylene terephthalate or a copolyester thereof for the reduction of the amount of acetaldehyde formed upon subjecting said moulding composition to melt processing, said hydroxylic compound being selected from aliphatic hydroxylic compounds containing at least two hydroxy groups, aliphatic-cycloaliphatic compounds containing at least two hydroxy groups, and cycloaliphatic hydroxylic compounds containing at least two hydroxy groups.

INTERNATIONAL SEARCH REPORT

Interna' al Application No
PCT/GB 00/01646

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K5/00 C08L67/02 C08K5/053 C08J3/205 //(C08K5/00, 5:053,5:13,5:3492,5:527)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Catogory °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 455 370 A (METACOL LIMITED) 6 November 1991 (1991-11-06) page 4, line 26 - line 27; example 8 ---	1-3,5,6, 15,16
A	EP 0 272 417 A (GEN ELECTRIC) 29 June 1988 (1988-06-29) page 2, line 13 - line 14 page 7, line 4 - line 14 claims 1,7,11,12,14; example 1 ---	1,3,15
A	WO 93 23449 A (ICI PLC ;GREAVES SARAH JENNIFER (GB); HARRISON DAVID ANTHONY (GB);) 25 November 1993 (1993-11-25) claims 1,3,6,7,12; examples 2-8 --- -/--	1,3,15

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 August 2000	14. 09. 2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk	Authorized officer

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 874 517 A (HUANG XIAOYAN ET AL) 23 February 1999 (1999-02-23) column 7, line 28 - line 29; claims 1,21,31-33 ---	1,8-13
A	US 5 308 892 A (ZICKLER DIETER ET AL) 3 May 1994 (1994-05-03) column 1, paragraph 1 -column 2, paragraph 2 column 4, paragraph 3; claims 1,8; example 1 -----	1,2,6-8

1

INTERNATIONAL SEARCH REPORT

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Internal Application No
PCT/GB 00/01646

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